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AN AUTOMATED GEL PERMEATION CHROMATOGRAPHIC METHOD FOR CLEANUP OF SEWAGE SLUDGE EXTRACTS FOR GC/MS ANALYSIS OF PRIORITY ORGANIC POLLUTANTS

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The increasing emphasis placed on water pollution and hazardous waste control, backed by stringent regulations such as Ontario's Municipal and Industrial Strategy for Abatement (MISA) program has increased the interest in the behaviour and fate of a wide range of organic contaminants during the wastewater treatment process. One result of this process is the annual production of approximately 7 million cubic meters of sludge. Treated sludges find many uses (1) including:

- co-disposal in landfill sites;
- agricultural land or land stabilization application;
- used as a fuel for low temperature incineration/power production;
- anaerobic digestion/evolution of methane gas;
- added to animal feeds (after suitable prescreening for contaminant levels).

Given these potential uses and the fact that many organic chemicals which enter wastewater treatment systems are ultimately retained in the sludge it is important to establish the nature and concentrations of these pollutants.

To satisfy the needs of investigative and regulatory environmental monitoring, the TO section of the LSB has been developing a rapid GC/MS method for the analysis of sewage sludges. Organic compounds investigated include:

- 40 base neutrals;
- 20 phenolics;
- 7 phenoxy acid herbicides;
- polychlorinated Biphenyls;
- 30 chlorinated hydrocarbons (pesticides and industrials).

These target organic compounds may be present in sludges (2) either in: solution, colloidal suspension, or absorbed on particulate matter.

This coupled with the chemical complexity of sludge, including high and variable organics and solids content, present major problems in the determination of trace levels of organic priority pollutants.

The objective of this research project was to develop an effective, and rapid analysis procedure which would quantitatively extract the target components, and consistently separate them from the co-extracted interferences including lipids, fatty acids, hydrocarbons and other high molecular weight compounds (3). Gel Permeation Chromatography (GPC) is a widely used technique in biochemical analysis and a large number of papers had been published [4-11] describing the cleanup of environmental sample extracts such as fish, sludge, solid waste, soil and sediments. In this regard the application of Gel Permeation Chromatography (GPC) was evaluated and an automated rapid cleanup procedure was devised.

Experimental

Apparatus - Shimadzu High Performance Liquid Chromatograph equipped with a SIL-6B Autoinjection (modified with a 2 ml injection loop) and Advantec SF-2120 Superfraction collector. Column - 600mm x 30mm packed with 60g of Bio-Beads SX3 (Bio-Rad Laboratories).

Elution Solvent - Methylene chloride-cyclohexane (1:1, V/V) flow rate 2 ml/min.

Calibration mixture - A standard mixture was prepared by dissolving Di-n-octylphthalate, Benzyl butyl phthalate, Methoxychlor and 4-nitrophenol in Methylene chloride (5µg/mL) of each compound).

Sample Preparation

Sewage sludge(s) varying in consistency from 0-20% solids was homogenized and a 25g portion was extracted with a mixture of solvents (Diethylether/methylene chloride 2:1, V/V). The extract was concentrated to 2 ml. A 0.5 ml extract was injected in the GPC system for cleanup.

Results and Discussion

- In our preliminary studies, two conventional open column chromatography cleanup approaches were evaluated using a Gel Permeation Chromatography (Bio-Beads SX) and polarity separation (Florisil).
- Qualitative GC/FID screening of the extracts cleaned on Bio Beads SX (collecting one fraction) do not appear much different from those of extracts cleaned up by Florisil Column Chromatography. Both of these extracts proved to be too complex (i.e. too much interfering material) to analyse by GC/MS.
- The cleanup on Bio-Beads SX was repeated employing an HPLC system.
- The packings and solvent system evaluated were:
 - Bio-Beads SX2 - Methylene Chloride
 - Bio-Beads SX3 - Methylene chloride/cyclohexane (1:1,V/V)
 - Bio-Beads SX8 - Methylene chloride/cyclohexane (1:1,V/V)
- Bio-Beads SX3 - gave the best results and was selected for further work.

Collecting all our target compounds in one fraction gave unsatisfactory results, so a fractionation procedure was developed. In order to calibrate the system and determine the optimum fractionation window size, the standard mixture was separated on the Gel Permeation Chromatography system.

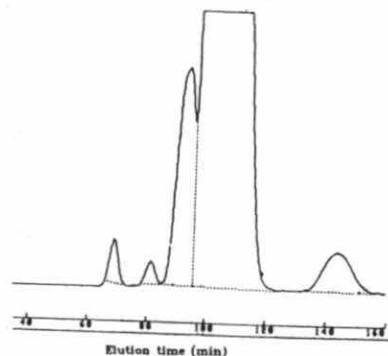


Fig. 1 - GPC elution profile of a standard mixture eluted with CH₂CL₂/CYCLOHEXANE (1:1) on Bio-Beads SX-3(60g)

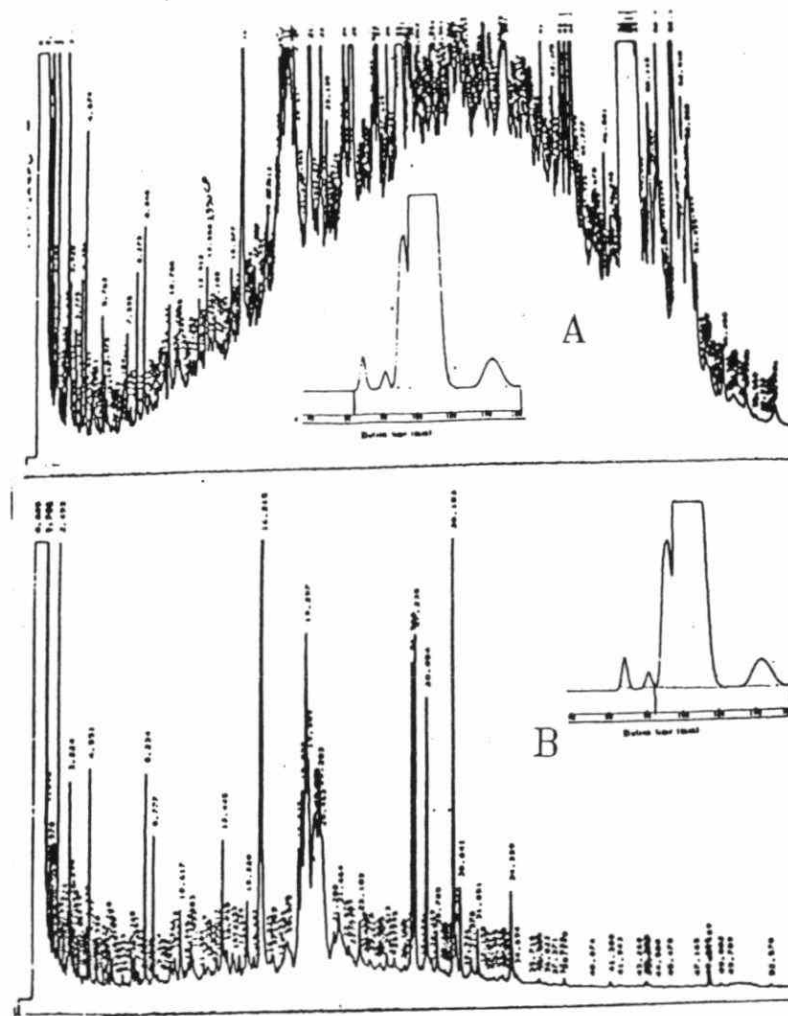


Fig. 2 - Flame ionization Gas Chromatograms of a sludge extract cleaned up by GPC: A - total collected, B - Fraction II

Two fractions were collected.

Fraction I from 62 min (when the first compound Di-n-octylphthalate elutes) to 82 min (at the valley between benzyl butyl phthalate and the Methoxychlor).

Fraction II collected from 82 min (when Methoxychlor elutes) to 157 min (after our last eluting compound 4-nitrophenol).

Fraction I contains all phthalates as well as the majority of interferences.

Fraction II contains all of the target compounds.

To illustrate the advantage of GPC fractionation procedure, see Fig. 2.

Summary and Conclusions

- This work is part of the effort to develop an analytical method for the determination of a wide range of organic contaminants in STP sludges.
- A number of GPC packing (Bio-Beads) for the cleanup of sludge extracts were investigated, ranging from SX3 to SX8.
- Bio-Beads SX3 were confirmed as the resin of choice for this type of work, in agreement with other researchers.

Sacrificial separation of a first fraction containing mainly phthalates virtually eliminated interferences from second fraction containing all other target priority pollutants.

- Separation conditions were optimized and then automated to provide an extract suitable for direct GC/MS analysis.
- The sacrificed fraction can be utilised for the analysis of phthalates after further cleanup on Florisil.

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